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## HEAT TRANSFER FLUIDS AND METHODS OF MAKING AND USING SAME

### Cross-reference to Related Applications

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This application claims priority from provisional patent application serial number 60/276,053, filed March 15, 2001, incorporated by reference herein.

### Background of the Invention

#### Field of the Invention

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This invention relates to novel compositions and their use as heat transfer fluids in a variety of applications.

#### 2. Related Art

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Pure or relatively pure helium has excellent heat transfer properties. For example, helium is typically employed to enhance fiber cooling during the optical fiber drawing process because it is chemically inert and because of its heat transfer properties. Of the common pure gases, only hydrogen has a higher thermal conductivity than pure helium. However, hydrogen is not as inert as helium and it is more hazardous to employ in certain gases related heat transfer applications than any inert gas. So, hydrogen is typically avoided as a gaseous heat transfer medium in some (but not all) cooling or heating process applications.

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Typical impurities in the helium used in heat transfer processes are due to minor impurities initially present within the source of "pure" helium as well as contamination by infiltration of other species into the helium that is used to transfer heat between the helium and the item or material being cooled or heated. These impurities often consist primarily of

nitrogen and oxygen with much smaller concentrations of argon, carbon dioxide, and water vapor as well as even smaller concentrations of other gaseous constituents normally found in air. These impurities are generally tolerated because they are difficult and/or costly to avoid, but they are not purposely introduced into the helium.

5 It is generally accepted that binary mixtures of helium (or hydrogen) with other gases will have better heat transfer coefficients than the pure gases themselves. See, for example, M.R. Vanco, "Analytical Comparison of Relative Heat-Transfer Coefficients and Pressure Drops of Inert Gases and Their Binary Mixtures, NASA TN D2677 (1965); F.W. Giacobbe, "Heat Transfer Capability of Selected Binary Gaseous Mixtures Relative to Helium and Hydrogen", *Applied Thermal Engineering* Vol. 18, Nos. 3-4, pp.199-206 (1998); R. Holoboff et al., "Gas Quenching With Helium", *Advanced Materials & Processes*, Vol.143, No. 2, pp.23-26 (1993). In particular, Holoboff et al. noted that in the context of a heat treating furnace, by changing to an optimum helium/argon mixture, a customer was able to heat treat parts that could not be processed as rapidly as using argon alone, while maintaining costs at a fraction of that for using 100% helium. In a separate example the same authors also recognized the benefits of increasing the fan speed (gas circulation velocity) on cooling rate for pure helium and for pure nitrogen. However, there is no teaching or suggestion of the influence of heat transfer fluid mixture velocity on cooling rate for optimized mixtures of heat transfer fluid.

20 For illustrative purposes, and according to earlier theories, the relative heat transfer capability of helium plus one other noble gas compared to pure helium may be seen in FIG. 1. In FIG. 1, pure helium has been arbitrarily assigned a relative heat transfer capability of 1.0 in order to deliberately avoid the use of a more complicated system of SI heat transfer units. Therefore, if a binary gas mixture containing helium has a heat transfer capability of 2.0 (relative to pure helium), it is assumed from this data that gas mixture will be 2.0 times more effective in any heat transfer process employing that gaseous mixture instead of pure helium alone. And, as a simplified illustration of the potential helium savings using this data, if the best binary gas mixture contained only 50 percent (by volume or mole fraction) helium plus 50 percent of some other gas, only 1/2 of that gas mixture would be needed to perform

the same cooling function as the pure helium alone. Therefore, only 25 percent of the helium that would have been required for a particular heat exchange process using pure helium would be needed during the same cooling process employing the gas mixture.

In FIG. 2, and also according to earlier theories, the optimum composition and approximate relative heat transfer capability of hydrogen plus one noble gas with respect to pure helium is illustrated. In FIG. 2, pure helium has also been arbitrarily assigned a relative heat transfer capability of 1.0. So, if a binary gas mixture containing only hydrogen and argon (but no helium) has a heat transfer capability of 1.4 (relative to pure helium), that gas mixture presumably will be 1.4 times more effective in any heat transfer process employing that gaseous mixture instead of pure helium alone. And, since no helium is required to produce this effect, the helium usage is cut to zero. Furthermore, since hydrogen and argon are typically much less expensive than helium, the overall cost of the hydrogen/argon coolant gas stream will tend to be negligible compared to a pure (or relatively pure) helium coolant gas stream.

It should be pointed out that the data presented in FIGs. 1 and 2 are theoretical and based on turbulent flow for the gases and gas mixtures considered. However, in the seminal work of R.B. Bird, W.E. Stewart, and E.N. Lightfoot, *Transport Phenomena*, pp. 392-393 (1960) it was pointed out that "the heat-transfer coefficient depends in a complicated way on many variables, including the fluid properties ( $k$ ,  $\mu$ ,  $\rho$ ,  $C_p$ ), the system geometry, the flow velocity, the value of the characteristic temperature difference, and the surface temperature distribution." In engineering design, therefore, use of constant property idealization frequently leads to either a greater built in safety factor, or a dangerous situation if the other extreme is taken. See D.M. McEligot, et al., "Internal Forced Convection to Mixtures of Inert Gases", *Int. J. Heat Mass Transfer*, Vol. 20, pp. 475-486 (1977).

Everyone agrees that helium is an expensive fluid. While it is inert, it is a non-renewable resource. Once it escapes to the atmosphere it is not recoverable. Helium is commonly recycled, sometimes after purification, such as described in U.S. Pat. Nos. 5,897,682 and 6,092,391. However this requires expensive compression and/or cryogenic

equipment. Indeed, as noted by K. Bammert et al., "The Influence of He-Ne, He-N<sub>2</sub>, and He-CO<sub>2</sub> Gas Mixtures on Closed-Cycle Gas Turbines", ASME paper 74-GT-124 (1974), while pure helium is often considered the best gaseous fluid in terms of heat transfer efficiency (except for pure hydrogen) and therefore heat exchange units may be particularly compact, the size of compression equipment required to compress the gas is prohibitive in many applications, such as space travel. Thus the expense of the heat transfer fluid (helium) is combined with a relatively large expense for compression equipment, even though heat transfer equipment may be smaller.

In light of the unexpected nature of heat transfer coefficients of fluids, it would be advantageous in many heat transfer situations common in engineering to employ a heat transfer fluid mixture that can easily be changed in composition to take advantage of the heat transfer properties of helium and/or hydrogen, without the great expense of pure helium and the expensive equipment needed to compress helium, while taking advantage of velocity effects on improvements in heat transfer performance.

### Summary of the Invention

In accordance with the present invention, a first aspect of the invention are heat transfer fluid mixtures consisting essentially of a heavy gas selected from the group consisting of nitrogen argon, carbon dioxide, and mixtures thereof, and a light gas selected from the group consisting of hydrogen, helium, and any mixture thereof. Preferred are heat transfer fluid mixtures wherein the light gas has a concentration ranging from about 20 mole percent to about 99 mole percent; more preferably wherein the light gas has a concentration ranging from about 30 mole percent to about 98 mole percent; more preferably ranging from about 40 mole percent to about 97 mole percent, more preferably ranging from about 50 mole percent to about 96 mole percent, and particularly heat transfer fluid mixtures having light gas concentration ranging from about 60 mole percent to about 95 mole percent.

A second aspect of the invention is a method of cooling an item, the method comprising contacting the item with one of the heat transfer fluid mixtures of the invention,

the contacting selected from the group consisting of directly contacting the item, indirectly contacting the item, and combinations thereof.

A third aspect of the invention is a method of heating an item, the method comprising contacting the item with one of the heat transfer fluid mixtures of the invention, the contacting selected from the group consisting of directly contacting the item, indirectly contacting the item, and combinations thereof.

A fourth aspect of the invention is a method of cooling an item traversing through a substantially confined space, the method comprising contacting the item with a heat transfer fluid mixture of the invention, the contacting selected from the group consisting of directly contacting the item, indirectly contacting the item, and combinations thereof.

A fifth aspect of the invention is a method of heating an item traversing through a substantially confined space, the method comprising contacting the item with a mixture of the invention, the contacting selected from the group consisting of directly contacting the item, indirectly contacting the item, and combinations thereof.

A sixth aspect of the invention is a method of cooling a substantially cylindrical item traversing through a substantially confined space, the method comprising contacting the substantially cylindrical item with a heat transfer fluid of the invention, the contacting selected from the group consisting of directly contacting the item, indirectly contacting the item, and combinations thereof.

A seventh aspect of the invention is a method of heating a substantially cylindrical item traversing through a substantially confined space, the method comprising contacting the substantially cylindrical item with a heat transfer fluid of the invention, the contacting selected from the group consisting of directly contacting the item, indirectly contacting the item, and combinations thereof.

An eighth aspect of the invention is a method of cooling a substantially cylindrical optical fiber traversing through a heat exchanger, the method comprising contacting the optical fiber with a heat transfer fluid of the invention, the contacting selected from the group consisting of directly contacting the item, indirectly contacting the item, and combinations thereof.

A ninth aspect of the invention is a method of improving the cooling of a substantially cylindrical optical fiber traversing through a heat exchange device, the method comprising the steps of:

a) contacting the optical fiber with a heat transfer fluid mixture of the invention, the contacting selected from the group consisting of directly contacting, indirectly contacting, and combinations thereof, and

b) making an adjustment, either intermittently or continuously, of a parameter during the cooling, the parameter selected from the group consisting of composition of the heat transfer fluid mixture, flow rate of the heat transfer fluid mixture into the heat exchange device, an amount of heat transfer fluid mixture contacting the fiber in counter-current fashion, an amount of heat transfer fluid mixture contacting the fiber in co-current fashion, composition of the heat transfer fluid mixture contacting the fiber in counter-current fashion, composition of the heat transfer fluid mixture contacting the fiber in co-current fashion, a temperature of the heat transfer fluid mixture being injected into the heat exchange device, a temperature of the heat transfer fluid mixture before contacting the fiber in counter-current fashion, a temperature of the heat transfer fluid mixture during contacting the fiber in counter-current fashion, a temperature of the heat transfer fluid mixture after contacting the fiber in counter-current fashion, a temperature of the heat transfer fluid mixture before contacting the fiber in a co-current fashion, a temperature of the heat transfer fluid mixture during contacting the fiber in a co-current fashion, a temperature of the heat transfer fluid mixture after contacting the fiber in a co-current fashion, a pressure of the heat transfer fluid mixture injected into the heat exchange device, a pressure of the heat transfer fluid mixture contacting the fiber in countercurrent fashion, and a pressure of the heat transfer fluid mixture contacting the fiber in a co-current fashion.

A tenth aspect of the invention is a method of improving cooling of an object in contact with a stagnant or flowing gas mixture in a confined space, the method comprising the steps of:

5 a) contacting the object with a heat transfer fluid mixture of the invention, the contacting selected from the group consisting of directly contacting, indirectly contacting, and combinations thereof; and

10 b) making an adjustment, either intermittently or continuously, of a parameter during the cooling process, the parameter selected from the group consisting of a composition of the heat transfer fluid mixture, a flow rate of the heat transfer fluid mixture in contact with the object, an amount of heat transfer fluid mixture contacting the object, a composition of the heat transfer fluid mixture contacting the object, a temperature of the heat transfer fluid injected into the confined space, a temperature of the heat transfer fluid mixture before contacting the object, a temperature of the heat transfer fluid mixture during contacting the object, a temperature of the heat transfer fluid mixture after contacting the object, a pressure of the heat transfer fluid mixture entering the confined space, and a pressure of the heat transfer fluid mixture contacting the object.

15 Preferred methods of this aspect of the invention are those wherein the parameter adjustment is made automatically or manually based upon a measured parameter of the object that changes during the cooling process.

20 An eleventh aspect of the invention is a method of improving heating of an object in contact with a stagnant or flowing gas mixture in a confined space, the method comprising:

a) contacting the object with a heat transfer fluid mixture of the invention, the contacting selected from the group consisting of directly contacting, indirectly contacting, and combinations thereof; and

25 b) making an adjustment, either intermittently or continuously, of a parameter during the heating process, the parameter selected from the group consisting of a composition of the heat transfer fluid mixture, a flow rate of the heat transfer fluid mixture in contact with the object, an amount of heat transfer fluid mixture contacting the object, a composition of the heat transfer fluid mixture contacting the object, a temperature of the heat transfer fluid

injected into the confined space, a temperature of the heat transfer fluid mixture before contacting the object, a temperature of the heat transfer fluid mixture during contacting the object, a temperature of the heat transfer fluid mixture after contacting the object, a pressure of the heat transfer fluid mixture entering the confined space, and a pressure of the heat transfer fluid mixture contacting the object.

Preferred are methods within this aspect of the invention wherein the parameter adjustment is made automatically or manually based upon a measured parameter of the object that changes during the heating process.

A twelfth aspect of the invention is a method of making a heat transfer fluid, the heat transfer fluid adjustable between a first composition having high heat transfer coefficient and high cost of use, and a second composition having essentially the same heat transfer coefficient as the first composition but allowing reduced cost of use, the method comprising the steps of:

- a) providing a light gas selected from the group consisting of hydrogen, helium, and mixtures thereof, from a light gas source;
- b) providing a heavy gas selected from the group consisting of nitrogen argon, carbon dioxide, and mixtures thereof, from a heavy gas source;
- c) ascertaining a heating or cooling demand; and,
- d) combining the light gas and the heavy gas based on the demand.

Preferred are methods wherein the demand is a cooling demand, and methods wherein the demand is a heating demand.



### Brief Description of the Drawing Figures

FIGs 1 and 2 illustrate the conventional belief that mixtures of helium with another noble gas, and mixtures of hydrogen with a noble gas, are always more effective heat transfer fluids;

5           FIG. 3A illustrates schematically an apparatus used to generate experimental data depicted graphically in FIGs. 3 and 4;

FIG. 3 illustrates graphically experimental data useful in the invention for helium/argon heat transfer fluid mixtures;

10           FIG. 4 illustrates graphically experimental data useful in the invention for helium/carbon dioxide heat transfer fluid mixtures; and

FIG. 5 illustrates a logic diagram useful in understanding the methods of the invention applied to a process of cooling an item such as an optical fiber.

### Description of Preferred Embodiments

15           Studies performed in our laboratories using gases showed that the heat transfer coefficient of gas mixtures varies with bulk velocity of the gas, and that there are certain mixtures of hydrogen and/or helium with argon and/or carbon dioxide and/or nitrogen that, at highly laminar and highly turbulent flow regimes, have poorer heat transfer properties than the pure light gas. However, it was determined that the heat transfer coefficients for gases containing a relatively high concentration of at least one "light gas", plus at least one "heavy  
20           gas" (such as argon, carbon dioxide or nitrogen) are higher than the heat transfer coefficient of the individual gas stream within a specific range of bulk velocities, referred to herein as the "critical bulk velocity range." Above or below this range of critical bulk velocities, the light gas stream will have a higher heat transfer coefficient.

As used herein, the words "light gas" and "heavy gas" refer (respectively) to a low molecular weight gas consisting essentially of hydrogen, helium or a mixture thereof, and a high molecular weight gas consisting essentially of nitrogen, argon, carbon dioxide, or a mixture thereof. The term fluid means either gas, liquid, or combination of gas and liquid. Furthermore, preferred heat transfer fluid mixtures of the invention are binary gaseous mixtures containing the lightest available "light gas" and the heaviest possible "heavy fluid", in just the right concentrations relative to each other, since these mixtures typically have the highest possible heat transfer coefficients (i.e., for cooling or heating purposes, they are the best gaseous heat transfer mediums).

In accordance with the present invention, and as mentioned previously, the inventor herein has discovered that certain mixtures of light gases and heavy gases may be employed that have substantially the same or better heat transfer (cooling or heating ability) as pure light or pure heavy gases. In particular, by simply measuring the bulk velocity of the heat transfer fluid mixture, a characteristic temperature difference of the system (either the mixture or the item being heated or cooled) and the heating or cooling demand, significant cost savings may be realized by the operator of the process or equipment utilizing the inventive heat transfer fluid mixtures. This may be seen by reviewing the data in FIG. 3. The curves in FIG. 3 were developed in the laboratory of the inventor using a laboratory set-up similar to that illustrated in FIG. 3A, which is now discussed.

Illustrated in FIG. 3A is an apparatus 1, having a copper tube 2 positioned concentrically within an outer stainless steel tube 4. There was thus a chamber between the inside surface of tube 4 and the outside surface of tube 2. Into this chamber was delivered steam through a steam inlet conduit 6 and steam exit conduit 8 sufficient to keep the inside and outside surfaces of tube 2 maintained at nearly 100°C. Copper tube 2 had a length between points A and B of about 9.4 inches (24 cm) between two thermocouples located in the center of the gas stream flowing there through. Copper tube 2 was 0.25 inch (0.64 cm) inside diameter, and about 0.5 inch (1.3 cm) outside diameter. Thermocouples 10 and 12 measured the temperature of entering and exiting steam, respectively, while thermocouples 54 and 62 measured temperature of inlet and outlet gas streams, respectively. Premixed

helium/argon gas streams tested entered tube 2 at nearly 0°C by virtue of having been cooled by an ice bath prior to entering tube 2, and all gases entered the tube at approximately 1 atmosphere pressure. Premixed gas streams entered apparatus 1 through a conduit 14 and valve 16, passing then through a gas flow rotameter as illustrated, although other types of gas flow meters could have been used just as well. Gas streams then passed through a screwed fitting 20, tee 24, and fitting 26. A gas pressure guage 28, connected via a fitting 22, allowed observation of pressure of the gas stream exiting flow meter 18. A smaller tee 27 and fitting 29 allowed connection of a conduit 34, and a fitting 30 allowed a thermocouple 32 to monitor temperature of the gas stream leaving flow meter 18. Conduit 34 allowed the gas stream to pass through a coil 36 which was submerged in an ice bath (about 0°C) maintained in an insulated vessel 38. After passing through coil 36 the gas stream, now cooled to about 0°C, passes through a conduit 40. Since the gas stream picks up some heat from the ambient while passing through conduit 40, the apparatus 1 included a tube 42 which was enclosed in an outer shell 44. A series of fittings 45 connected tube 42 to copper tube 2, with thermocouple 54 positioned centrally in both tubes. Cold water from the ice bath in vessel 38 was pumped using a pump 50 through a conduit 48, into the chamber created between outer shell 44 and tube 42. Temperature of the cold water was monitored by another thermocouple 13. After being slightly warmed (as evidenced by a thermocouple 56) by indirect heat exchange with the gas stream flowing countercurrently through tube 42, the water was returned to vessel 38 through conduit 46. Pump 50 was provided with cold water from vessel 38 through another conduit 52. Gas temperature flowing between points A and B in copper tube 2 was monitored at various flow rates and gas compositions.

As can be seen in FIG. 3 for the helium/argon heat transfer fluid mixture, where helium is the light gas and argon the heavy fluid, at a bulk velocity through the tube below about 60 SCFH, the heat transfer fluid mixtures all had poorer heat transfer coefficients (as measured by the characteristic temperature difference defined as the temperature increase of the fluid) than pure helium. However, FIG. 3 also shows that at bulk flow rates between about 90 SCFH and 250 SCFH, mixtures of helium and argon, containing more than about 60 mole percent helium, performed almost as well as, or better than, pure helium alone.

FIG. 4 is a similar analysis for mixtures of carbon dioxide and helium. Notice that at flow rates below about 250 SCFH, and above about 80 SCFH, mixtures of helium and carbon dioxide, containing at least 60 mole percent helium, performed as well as, or better than, pure helium alone.

5           Mixing of light gases with heavy gases may be done by any number of means and is not critical to the present invention. One preferred process and apparatus is described in copending application serial number 09/764,424, filed January 19, 2001, "Apparatus and Method for Mixing Gases", incorporated by reference herein. In the processes of the '424 application, a gas mixing apparatus produces a flow of a gas mixture. The gas mixture can be used in various applications of the present inventions and can preferably supply one or more points of use.

10           The flow of the gas mixture from the gas mixing apparatus to one or more points of use is typically continuous. However, the flow may be interrupted for particular purposes such as, for example, maintenance, quality control and/or safety purposes.

15           The mixing apparatus produces a gas mixture comprising at least two gases. For example, the apparatus can produce, but is not limited to producing, a gas mixture comprising the following gases: nitrogen and hydrogen; nitrogen and helium; argon and helium.

20           The preferred mixing apparatus of the '424 application can effectively provide a gas mixture having an increased consistency in mixture concentration. For example, in a hydrogen and nitrogen mixture in which the intended hydrogen concentration is 3% by volume and the nitrogen concentration is 97% by volume of the mixture, the apparatus 100 can typically maintain the hydrogen concentration of the mixture at about  $3\% \pm 0.15\%$  by volume of the mixture.

25           The preferred mixing apparatus includes a first gas source that is connected to introduce a flow of a first gas or gas mixture into a gas mixing manifold. A second gas source is connected to introduce a flow of a second gas into the gas mixing manifold. The flows of the first and second gases into the gas mixing manifold are preferably continuous.

Valves are normally in an open position to permit flow of the first and second gases therethrough, respectively. The first and second gases are mixed in the gas mixing manifold, thereby forming a gas mixture. The first and second gas sources are preferably located on-site, for example, at a metal heat treating facility.

5           The gas sources may be bulk gas sources. For example, bulk gas sources can have a volume from about 40,000 ft<sup>3</sup> (1,130,000 liters) to about 20,000,000 ft<sup>3</sup> (5.66 x 10<sup>8</sup> liters). The bulk gas source can include, for example, a bulk gas container located at a manufacturing facility, or a gas-transporting tube trailer. Tube trailers typically have a volume from about 40,000 ft<sup>3</sup> (1,130,000 liters) to about 140,000 ft<sup>3</sup> (3,960,000 liters).  
10       Using a bulk gas source might supplement or replace a gas cylinder. As used herein, the term "gas cylinder" includes a gas container having a volume that is less than the volume of the bulk gas source, for example, from about 220 ft<sup>3</sup> (6230 liters) to about 300 ft<sup>3</sup> (8500 liters).

15           Preferred mixing apparatus can produce a flow of a gas mixture over a wide flow rate range. The flow rates of the flows of the first and second gases depend at least on the amount of heat transfer fluids desired and/or the desired concentration of the first and second gases in the heat transfer fluid (HTF) mixture.

20           Under normal process conditions, a point of use for a HTF mixture receives a continuous flow of the HTF mixture from the gas mixing manifold. Under particular process conditions, however, the flow of the gas mixture to the point of use is stopped. Such process conditions can include, for example, the non-operation of the point of use, such as when a processing apparatus is shut down for maintenance or production is otherwise stopped, and/or when the HTF mixture does not comply with desired specifications. The flow can be  
25       stopped by closing a normally-opened three-way valve such that the flow to the point of use is stopped.

          According to the preferred embodiment, particular components of the preferred mixing apparatus include such as, for example, first and second mass flow controllers.

The temperatures and pressures of the gases through the preferred HTF gas mixing apparatus typically depend upon the types of gases used and/or the particular heat transfer application of the gas mixture. For example, in the production of a nitrogen and hydrogen HTF mixture, the pressure of the nitrogen gas flow is preferably about 110 psig, and the pressure of the hydrogen gas flow is preferably about 120 psig. The preferred apparatus can optionally include one or more regulator that adjusts the pressure of the gas flow provided by the first and/or second gas sources.

According to a preferred embodiment, the flow rate of the first and second gases can be regulated by first and second mass flow controllers. The flow rates depend, for example, on the desired flow rate of the HTF mixture product stream, the desired concentrations of the first and second gases of the gas mixture, and the particular HT application of the HT gas mixture.

The HTF gas mixture exiting the gas mixing manifold can optionally be introduced to a buffer vessel. The buffer vessel functions as a container for the HTF gas mixture product, and is formed of a material suitable for containing the gas mixture such as, for example, stainless steel. In a preferred embodiment, the buffer vessel has a volume of about 25 gallons (94.6 liters). The gas mixture can be removed from the buffer vessel and introduced to the point of use.

At least one filter can optionally be included in the HTF gas mixing apparatus to reduce the level of impurities in the gas mixture product. For example, according to a preferred embodiment, the heat transfer mixing apparatus can optionally include filters to reduce the amount of impurities in the gas flows introduced from the first and second gas sources.

The preferred mixing apparatus can optionally include a controller which can adjust the concentration of the gas mixture, for example, by monitoring and controlling the flow rates of the first and/or second gases. The controller can adjust the concentration of the gas mixture by adjusting at least one of the mass flow controllers. Suitable controllers and

control methods are known to those skilled in the art. The controller can be, for example, a programmable logic controller (PLC).Op

According to a preferred embodiment, the controller can be programmed to provide a gas mixture having a desired concentration by adjusting at least one of the mass flow  
5 controllers. A detector and a gas analyzer can measure the concentration of at least one gas in the gas mixture and can provide this information to the controller 200. Preferably, the concentration of the heat transfer gas mixture is measured proximate to the point of use. For example, in a preferred embodiment, the controller can determine the concentration of the first and second gases in the gas mixture. One or both of the first and second mass flow  
10 controllers can then be adjusted to regulate the overall concentration of the gas mixture.

At least one additional sensor and/or detector can measure various characteristics of the gases flowing through conduits of the apparatus including, for example, pressure, flow rate, temperature and/or concentration of the gases. The information from the additional sensor(s) and/or detector(s) can be received and processed by the controller. The controller  
15 can also provide a data report that includes, for example, information relating to the various pressures, flow rates, temperatures, and gas mixture concentrations of the gases. The status of the apparatus can be monitored from a remote location, thereby reducing or eliminating the need for daily monitoring through human interaction.

In a preferred embodiment, the gas analyzer is a hydrogen gas analyzer such as, for  
20 example, the AT-401 percent hydrogen analyzer available from Thermco Instrument Company located in Laporte, Indiana. The gas analyzer is typically connected to receive a flow of a span gas, i.e., a reference gas. The span gas is typically used to calibrate the gas analyzer. The concentration of the span gas typically corresponds to the desired concentration of the gas mixture product. The gas analyzer is also typically connected to  
25 receive a flow of a purge gas from a purge gas conduit. The purge gas can be, for example, nitrogen.

Preferably, when the heat transfer fluid mixtures of the invention are employed for cooling, they are at moderate temperatures cooler than the object to be cooled or frozen, for example preferably entering the cooling device or area at no more than ambient temperature

(about 25°C), and preferably no higher than about 0°C. When used for heating applications, the inventive heat transfer fluid mixtures preferably enter the heating device or area heated to a temperature above the demand temperature, but below the decomposition temperature of the heavy gas. Very low temperatures, for example, may tend to cause condensation of one or more gases in a mixture and this may not be beneficial insofar as gaseous heat exchange is concerned unless this kind of process is intended as in "heat pipes".

Alternatively, very high temperatures may cause the decomposition of carbon dioxide in a mixture during a heat exchange process and adversely affect the overall efficiency of the intended heat exchange process due to an unintended change in the original gas mixture composition.

In general, the heat transfer fluid mixtures of the invention are beneficial in any system where a moving or non-moving item is intended to be heated or cooled, either through direct contact with the mixture, or indirect contact such as through a heat exchanger tube wall. In the optical fiber drawing art, the fiber typically moves through a heat exchanger and the gas mixture directly contacts the fiber (see for example FIG. 1 of US Patent 6,125,638, incorporated herein by reference for its teaching of an optical fiber cooling heat exchanger). While the heat transfer coefficient of a gas flowing past a stationary cylinder has been defined, for example as discussed in Holoboff et al. "Gas Quenching With Helium", Advanced Materials & Processes, February 1993, there are uncertainties involved in any particular heat transfer system that make prediction difficult. For example, in the fiber drawing art, the optical fiber is moving through a heat exchanger, being drawn by a spool. In one method, the coolant gas typically enters the exchanger at about the mid-point of the fiber in the exchanger, and then splits, some of the gas traveling co-currently with the fiber, and some traveling counter-currently in relation to fiber flow direction, as depicted in the 638 patent.

FIG. 5 illustrates one preferred version of a logic diagram 10 for using the inventive heat transfer fluid mixtures of the invention for a heating or cooling process. The particular process is not important to this discussion. More specific examples are offered in the Examples section that follows. First, the light gas and heavy gas are selected, as depicted in boxes 12 and 14. For the moment and for ease of explanation, it will be assumed this is a



two-component, or binary heat transfer fluid (HTF) mixture. As discussed herein, depending particularly on the heavy gas, this ideal may be a simplification that is not true, for example when the heavy fluid is exposed to conditions that would decompose some or all of the heavy gas. The selection is chosen based on known properties of the item or fluid to be heated or cooled. For example, if the item is a food item to be frozen, then the light gas and heavy gas would be selected from "generally recognized as safe" food grade hydrogen or helium, or mixture thereof, and heavy gas, for example argon, carbon dioxide or mixture thereof.

If the heat transfer process is heat treatment of metal items, the selection is made based on the desired end properties of the metal. An initial HTF mixture is then prepared, either manually or through a computer controlled operation, remotely or locally, as depicted at 16, perhaps an 80 mole percent light gas/20 mole percent heavy gas mixture. A determination is made of the cooling or heating demand for the item being heated or cooled, as illustrated at 18. This determination could be as simple as a human operator decision based on previous experience, or as complex as a computer-controlled thermal analysis using a variety of temperature sensors, feed-forward information on the characteristics of the incoming material to be heated or cooled, and the like.

Once a determination of demand is made, flow of HTF mixture is initiated, as indicated at 20, and a characteristic temperature difference, or  $\Delta T$ , is measured. The characteristic  $\Delta T$  could either be based on temperature change of the HTF mixture between an entering point and an exit point of the heat exchange unit, or temperature change of the item being heated or cooled, or a combination. An example of a combination would be, for example, when heat-treating metals. Initially the temperature rise of the metal might be monitored, and then, typically, the temperature of the metal piece is maintained at a certain temperature for minutes or hours. In these circumstances, the

$\Delta T = 0$  for the metal, so  $\Delta T$  of the HTF mixture is monitored.

Next, two questions are asked as depicted in the diamond boxes 24 and 26. The first question 24 is whether the heating or cooling demand is being met. If the answer is "yes", the sequence moves to the second question, and asks if the cost of meeting the demand is

within acceptable limits. If the answer to this question is “yes” the HTF mixture is performing as intended in accordance with the invention, and the  $\Delta T$  is measured again, and the two questions at 24 and 26 are asked again, and so on.

Returning to diamond box 24, if the heating or cooling demand is not being met, then the composition and/or bulk velocity (BV) of the HTF mixture is changed, in accordance with a chart such as illustrated in FIGs. 3 and 4, and the characteristic  $\Delta T$  is measured again, and the question is asked again, until the heating or cooling demand is being met. If the second question, as depicted in diamond box 26 is answered “no”, then again the logic is that the composition and/or BV of the HTF mixture is modified, in accordance with a chart as in FIGs 3 and 4, and the two questions are asked again.

One will recognize, after reviewing this disclosure, that the logic of FIG. 5 does not imply that there ever will be a constant composition of the heat transfer fluid mixture (although this condition is not outside the scope of the invention); indeed, understanding this point largely explains a key aspect of the invention. There will tend to be a struggle between cost and meeting the demand.

Another option is to add a third (or more) component to the HTF mixture, as depicted in box 30. Behavior of a mixture containing, for example, two heavy fluids and one light fluid are expected to have heat transfer characteristics similar to an average of the two heavy fluids and the light fluid.

The following examples demonstrate the range of use of the HTF mixtures and methods of the invention.

## Examples

### Example 1. Heat Treatment of Metal Parts

A conventional annealing furnace of the continuous type could be adapted for use with the present invention. For example, 800 feet of a 0.100 inch thick, 25 inch wide strip of unalloyed zirconium could be annealed. The heat transfer fluid mixture used could be made by combining liquified argon stored at a tank pressure of 22 psig with helium, for example by

vaporizing the argon into a line through which helium is flowing. The mixture would be delivered about 15 inches above the product path in the hot/work zone. The mixture could be delivered to the chamber in an approximately 70/30 helium/argon mixture. About 0.5 to about 5.0 lb./min. of mixture would be introduced into the hot/work zone, resulting in a nominal furnace chamber pressure of about 0.8 psig with goal of obtaining a residual furnace oxygen concentration of about 10 ppm after about 20 minutes.

The temperature of the hot/work zone is then typically increased from a starting temperature of about 400.degree. F. to an operating temperature of about 1600.degree. F. through the use of electric heating elements. The mixture flow is monitored in order to quantify suitable operating parameters and in order to stabilize the pressure over the hot/work zone. These adjustments are typically successful in keeping residual oxygen levels between about 5.8-10 ppm without having to exceed chamber pressures of 2 psig.

#### Example 2. Freezing of Food and Other Materials

Cryogenic individual quick freeze (IQF) freezer apparatus may be used in practice of present invention. IQF provides an apparatus which employs cryogenic liquid to efficiently crust freeze or fully freeze food products or other industrial products (such as rubber spheres and the like) of small to medium size (from about 1 millimeter diameter to about 5 centimeters in diameter for roughly spherical items, such as plums). The food or other industrial product is preferably of a size and shape such that it can be moved in two or three dimensions. For example, food products that may be IQF by the freezer apparatus of the invention include shrimp, peas, diced meat, and meatballs. Examples of products that probably would not be preferred include hamburger patties, packaged food, and, due to the fragility and dimension ratios, products like tortillas and potato chips.

Freezer apparatus would preferably use direct contact of heat transfer fluids of the invention to cool the product as it travels through a freezing chamber along a product support, preferably employing a moving conveyor belt. It should be understood, however, that a moving conveyor belt is not necessary in all embodiments; a stationary table can be used. This is because in some preferred embodiments a plurality of blowers are positioned on either side of product support to agitate the product, move the product across the product

support, and to cool the product as it passes through freezing chamber from a product entrance to a product exit.

In preferred embodiments wherein cryogenic liquid is sprayed directly onto a freezing chamber, a freezer housing completely encloses and contains the cool cryogenic gas so that the only openings provided are a product entrance and a product exit at either end of freezer apparatus.

Blowers mounted in recirculation chambers preferably each have an inlet preferably on the upper surface thereof and an outlet in one of side walls of the freezing chamber. Blowers draw the cold gas from freezing chamber through gaps between the top of side walls and a top cover and recirculate the cold cryogenic gas across the product on conveyor belt. Blower outlets direct the cryogenic liquid (or cold air in mechanical-type apparatus embodiments) laterally across the conveyor belt directly on the product, causing the product both to be cooled and to be agitated or blown across and/or over conveyor belt at the same time by the force of the gas. In embodiments where cryogenic liquid is sprayed directly into the freezing chamber, the liquid cryogen injectors are preferably positioned in the blower exits of the first blowers. Blowers may be single speed or variable speed, depending on factors such as product size and shape, whether two dimensional or three dimensional translation is desired, and the like. Although it is possible to use single speed motors in the blowers, it is more preferable to employ variable speed "squirrel cage" blowers. A variable speed blower having a 2 horsepower motor with a 13.5 inch (34.3 cm) radial blade rotating at 1725 rpm is sufficient to agitate a plurality of individual product pieces, each having an average diameter ranging from about 0.5 centimeter up to about 5 centimeters, and density ranging from about 0.7 to about 2.0 grams per cubic centimeter, across an 18 inch (45.7 cm) wide horizontal conveyor belt. Blowers of this and other sizes are available from Dayton Blower Co., Dayton, Ohio. Liquid cryogen injectors spray the cryogenic liquid directly on the food or other products that are passing along conveyor belt in front of the blower outlets.

It is understood that if a non-food product is to be IQF, even heat transfer fluids not acceptable to the food industry may be used. Furthermore, the liquid cryogenic injectors may be replaced with mechanical cooling methods. Heat transfer in these embodiments occurs between the air in the freezer chamber and the refrigerant in the cooling coils. In these

embodiments, blowers preferably move air, although it is possible to also spray heat transfer compositions of the invention into the freezer chamber at the same time that mechanical cooling is employed.

#### Example 3 Freezing of Foods

5 U.S. Pat. No. 5,921,091, incorporated by herein by reference, discloses an example of a straight tunnel freezer which may benefit from the teachings of the present invention. As illustrated in FIG. 1 of the 091 patent, a straight tunnel freezer includes an elongated freezer tunnel and a conveyor on which a food product is transported from a freezer entrance to a freezer exit. One or more coolant nozzles are provided within the tunnel, preferably near the entrance of the tunnel. Coolant nozzles would direct a mixture in accordance with the invention directly onto the product. Alternatively, coolant nozzles may be provided in the tunnel without directing the coolant directly on the food product. In this case, the cool gas mixture within the tunnel is circulated around the food product by means of fans or blowers. One or more fans may also be provided within the tunnel either above, below or at a side of the conveyor belt for circulating the cold gases within the freezer.

10 The 091 patent teaches the use of mixtures of oxygen and nitrogen to form "synthetic air". In the present invention, preferably a mixture of helium and carbon dioxide would be used. The amount of helium provided from a helium supply and an amount of carbon dioxide from a carbon dioxide source would be controlled by flow control valves 26, 28. Valves 26, 28 may be controlled by a controller 30 to achieve the desired cryogenic mixture, preferably of 18% to 25% oxygen. Valves 26, 28 may also be controlled manually.

#### Example 4. Cooling of Optical Fibers

25 Production of optical fibers typically employs helium or hydrogen to dry glass preforms during consolidation, for drawing the fiber during heating, and for cooling the drawn fiber, especially if the fiber is to be coated with a resin for toughening the fiber, and making it more resistant to fatigue, abrasion, and the like. US Pat. No. 6,092,391 discloses some details of a consolidation furnace. This patent discloses the use of a sensor (either composition, P, T, or flow rate) on the exhaust stream. Another patent, US Pat. No. 5,284,499, discloses how a glass

preform is drawn through a heating element, a diameter measuring device, and a muffle tube. The cooling gases (helium or argon) flow into the top of the tube in this arrangement, and is heated as it passes into contact with the fiber, which is typically at a temperature of about 2100 – 2300°C. The fiber is typically drawn under tension of about 9 grams, at a draw rate of about 9  
5 meters/second. The gas flow rate is disclosed to be about 3 slpm. In this patent, it is preferred to keep a boundary layer of gas near the fiber to thus maintain the boundary layer and prevent air currents, which might produce "bow" (fiber bending) and "airline" (small holes in the fiber).

Other patents in the area of optical fiber manufacturing interestingly call for more  
10 turbulent flow of the gas to cool the fiber as quickly as possible so that resins may be applied. Representative of this is US Pat. No. 4,437,870. The first mention of helium used in optical fiber manufacture as a coolant appears to be US Pat. No. 4,154,592, where it was recognized that helium apparently reduced thermal gradients due to its higher thermal conductivity compared to oxygen and nitrogen. Mixtures of helium/oxygen/nitrogen were discussed.  
15 Another interesting patent is US Pat. No. 5,059,229, which discloses the use of helium/hydrogen mixtures, but no mention of the heat transfer effects. The point was to introduce hydrogen into the coolant gas to prevent "transient hydrogen sensitive attenuation." There was no recognition in any of these patents of heat transfer fluid mixtures that could be changed in composition and/or flow rate (bulk velocity) to achieve both lower cost and more  
20 effective cooling.

The present heat transfer fluid mixtures can be advantageously employed in optical fiber consolidation, drawing, and fiber cooling to decrease costs while achieving almost the same cooling as pure helium. Depending on the process, the light gas is first selected, for example helium, then a heavy fluid, such as argon, and the cooling demand determined. The  
25 composition is then adjusted, either by adding more argon or more helium, or an optional third fluid, such as carbon dioxide, and/or by adjusting the bulk velocity, and the cost also calculated for operating using the adjusted gas composition. If the cooling demand is still being met, and the cost is within acceptable limits, the adjusted gas composition and bulk velocity is maintained. If not, they are changed. The changes employ a computer stored  
30 version of the heat transfer data for example as depicted in FIG. 2 for the argon/helium system.

